

Structure OF WO_x/TiO₂ Catalysts Prepared From Hydrous Titanium Oxide Hydroxide: Influence of Preparation Parameters

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Tungstated titania catalysts (WO_x/TiO₂) were prepared by wet impregnation of hydrous titanium oxide hydroxide. The influences on the catalyst structure of tungsten loading (in the range of 0–30 wt% WO₃ supported on TiO₂), calcination temperature (varied from 473–973 K), and the form of the applied tungstate precursor (ammoniummetatungstate or ammoniummono-tungstate) were investigated by surface area measurements, X-ray diffraction, thermal analysis, temperature-programmed reduction, vibrational and UV/VIS spectroscopy, and X-ray absorption spectroscopy. The data show that tungsten loadings giving higher than monolayer coverage of the TiO₂ and the application of a high-surface-area titania precursor lead to new structural properties of the surface tungstate phase. A tungstate overlayer is formed that is stable at loadings up to ca. two monolayers (20 wt% WO₃/TiO₂) at a calcination temperature of 923 K. Two tungstate species are characterized by two W=O bands in the vibrational spectra. One tungstate species shows a strong dependence of its domain size and degree of condensation on calcination temperature and tungsten loading, but the other does not. The first is attributed to accessible outer segments of a three-dimensional tungstate structure and the latter to the interface providing the linkage to the TiO₂ support. A three-dimensional structure is formed even at low tungsten coverages. This tungstate overlayer retards the sintering of the TiO₂ support and its phase transformation from anatase to rutile. With increasing tungsten loading, the surface area increases and the TiO₂ particle sizes and pore diameters decrease. When the tungsten loading exceeds 20 wt% WO₃ and the calcination temperature exceeds 923 K, WO₃ is formed. These results help to explain the properties of these materials including acidity, reactivity in reduction and isotope exchange, and catalytic activity.